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6. AUTHOR(S) Lorraine Falter Francis				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Minnesota Department of Chemical Engineering & Materials Science 421 Washington Ave. S.E. Minneapolis, MN 55455		8. PERFORMING ORGANIZATION REPORT NUMBER		
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13. ABSTRACT (Maximum 200 words)  The goals of this research project were to develop processing methods for fabrication of porous oxide coatings with a range of pore contents and to develop characterization methods for porous coatings. Research focused on controlling porosity in coatings prepared by the deposition of metal alkoxide solutions and coatings formed by a low temperature chemical reaction between alumina and phosphoric acid. The effect of processing conditions on pore content and pore size were established. Results can be divided into three categories: (1) development and control of porosity in alkoxide-derived titania coatings; (2) characterization of macroporous coatings and (3) porosity in alumina/aluminum phosphate coatings. Two categories of results concern the development of new processing methods for ceramic coatings and the scientific understanding of porosity control. The second category is a new method for the easy characterization of pore content in macroporous coatings.				
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PROCESSING AND CHARACTERIZATION OF POROUS OXIDE COATINGS

FINAL PROGRESS REPORT

LORRAINE FALTER FRANCIS

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## **PROBLEM STUDIED:**

The goals of this research project were to develop processing methods for fabrication of porous oxide coatings with a range of pore contents and to develop characterization methods for porous coatings. Research focused on controlling porosity in coatings prepared by the deposition of metal alkoxide solutions and coatings formed by a low temperature chemical reaction between alumina and phosphoric acid. The effect of processing conditions on pore content and pore size were established.

## **SUMMARY OF IMPORTANT RESULTS:**

Results can be divided into three categories: (1) development and control of porosity in alkoxide-derived titania coatings, (2) characterization of macroporous coatings and (3) porosity in alumina/aluminum phosphate coatings. Two categories of results concern the development of new processing methods for ceramic coatings and the scientific understanding of porosity control. The second category is a new method for the easy characterization of pore content in macroporous coatings. Below, important results in these categories are summarized below.

### **1. Development and Control of Porosity in Alkoxide-Derived Titania Coatings**

One of the most important results of this research program was the development of a new processing route for porous titania coatings. Anhydrous titanium ethoxide/alcohol solutions are spin coated onto substrates and then heated for crystallization (typically  $\sim 500^{\circ}\text{C}$ ). Atmospheric moisture rapidly reacts with the Ti ethoxide during coating, forming colloidal particles ( $\sim 100\text{-}300\text{ nm}$ ) when the relative humidity is high enough and the concentration low enough. Complete particle formation maps were constructed to show the processing window for particle formation in terms of the main experimental variables (humidity, alkoxide concentration in the coating solution, and spin coating rate). Particles are the building blocks for the porous coating; porosity is controlled by the agglomeration of these particles and the packing of the agglomerates. Processing conditions affect the agglomeration process and hence porosity. For example, increasing the spin coating rate from 2000 to 8000 rpm decreases the porosity from 50 to 32% and average pore size from 1.7 to 0.9  $\mu\text{m}$ . Faster spinning rates lead to less time for agglomeration, and therefore smaller agglomerates which pack better. Coatings were typically prepared by multiple deposition to create coating that were 1-10  $\mu\text{m}$  thick.

The fundamentals of porosity control in coatings prepared from particle forming alkoxides solutions were detailed. Particle formation via reaction with atmospheric moisture was found to follow similar behavior as particle formation in bulk solutions containing water, alkoxide and alcohol; however, the special conditions of coatings can not be achieved bulk solution. The roles of solution concentration, relative humidity and spin coating rate on particle formation, agglomeration and coating pore structure were determined. These three variables allow one to create coatings with pore contents ranging from 30 to 60% and average pore sizes ranging from submicron to  $\sim 3\text{ }\mu\text{m}$ . By adding a steric stabilizer to the coating solution, agglomeration was prevented, denser coatings were prepared and the pore size distribution narrowed considerably. A relationship between microstructure and the development of crystalline structure on heating was found. Porous coatings containing large, loosely connected particle clusters transformed from the anatase to the rutile structure at lower temperatures than denser coatings. The relief of the stress associated with the transformation was possible in porous, but not dense coatings.

Previous technical progress reports and publications provide details on the processing - microstructure relationships. The control of microstructure in coatings that produce particles during deposition has general implications. The wide range of microstructures achieved in titania coatings provides an example; any coating system that has a reaction to form particles during deposition could be manipulated in a similar way. For example, zirconia coatings with similar microstructures can be prepared with Zr alkoxides. The research also drew attention to an often overlooked processing variable: relative humidity. Finally, one may consider achieving similar changes in microstructure in multiphase coatings as well. For example, a dispersion can be prepared with a particle phase and in a liquid that contains reactive precursors that precipitate during deposition; the coating would then be composed of two types of particles with the possibility of controlled phase distribution.

## **2. New Characterization Methods for Macroporous Ceramic Coatings**

Characterization of the pore structure of coatings is a challenging task. Usually researchers rely on SEM to verify that their coatings are porous and to characterize the pore size. Pore content is difficult to determine using SEM. In this research project, a simple gravimetric method was developed to determine the pore content of ceramic coatings. The procedure involves filling the coating's pore space with a liquid and measuring the weight loss on volatilization of the liquid with a thermogravimetric analyzer. This thermogravimetric volatilization of liquids (TVL) method was used to characterize the porosity in a variety of coatings. The measured porosities of the ceramic coatings ranged from 30 - 80%. The method was most effective on coatings that were thicker than around 20 $\mu$ m. Errors involved with the removal of excess liquid prevented accurate measurements of thinner coatings. Porosities determined by TVL were within 5-10% of those determined by mercury intrusion porosimetry on identical samples. The TVL method has advantages: it is non-destructive, can be used for small volumes of sample, and when combined with SEM, provides a good means to characterize coating porosity and pore structure. A full description of the method can be found in a publication.

## **3. Development and Control of Porosity in $\text{Al}_2\text{O}_3/\text{AlPO}_4$ Coatings**

The second processing route developed in this research involved bonding together alumina particles in a porous coating with an aluminum phosphate reaction product. Similar to the work on titania coatings, the goal was to tailor the microstructure of a porous ceramic coating. In this phase of the research, emphasis was also placed on lowering the processing temperature to make deposition on a wider range of substrates possible and increasing the strength of coating. This coating system was investigated to act as a ceramic matrix for ceramic composite coatings needed in a related ARO project funded by the AASERT program. Coatings were prepared by depositing a aqueous dispersion of alumina particles containing phosphoric acid and sometimes aluminum chloride. The amount of phosphoric acid added was varied to provide dispersions with  $\text{H}_3\text{PO}_4$  : alumina weight ratios of 0.0106:1 to 0.106:1. Another set of dispersions was prepared with a  $\text{H}_3\text{PO}_4$  :  $\text{Al}_2\text{O}_3$  weight ratio of 0.106:1 and with aluminum chloride added in an amount ranging from 0.001:1 to 0.1:1 ( $\text{AlCl}_3$ : $\text{Al}_2\text{O}_3$  by weight). Coatings were dried in air overnight and then heated at either 100°C- 500°C. Coating were typically 30  $\mu$ m thick, but could be prepared with a wide range of thicknesses.

The composition of the coating dispersion and the thermal treatment controlled the ceramic phase connectivity, coating porosity and coating strength. Reactions ensue and affect the phase composition as well as the microstructure of the coating. For coatings prepared with alumina and phosphoric acid, alumina reacts with phosphoric acid to form hydrated aluminum phosphate phases at ~300°C; crystallization of the reaction product occurs at higher

temperature. For coatings prepared with aluminum chloride, the aluminum chloride initially reacts with water to form aluminum hydroxide which then reacts quickly with phosphoric acid to form aluminum phosphate. The phosphoric acid content controlled porosity and microstructure features in coatings prepared with alumina and phosphoric acid. Increasing the acid content from led to rounding of the alumina particles, the formation of greater amounts of aluminum phosphate as bridges between particles and a reduction in the porosity from 50 to 30% . The effect of acid loading on porosity can be understood considering the density difference between aluminum phosphate and alumina ( $2.56 \text{ g/cm}^3$  vs.  $3.98 \text{ g/cm}^3$ , respectively). For a given temperature, coatings with larger acid loadings form more aluminum phosphate and are denser (i.e., the conversion of a high density solid to a low density solid consumes pore space). The coatings with more acid were also more robust. Porosity measurements also revealed that the pore content of the coating was invariant to the aluminum chloride addition. In the preparation of the coating dispersion, aluminum chloride reacts with water in the alumina dispersion to form aluminum hydroxide particles; these fine particles react with phosphoric acid when it is added to the dispersion. The result is formation of aluminum phosphates before deposition and less conversion to phosphate takes place in the solid coating.

Porous ceramic coatings with pore contents ranging from 25 to 50% were prepared at processing temperatures as low as  $300^\circ\text{C}$ . The porosity in coatings prepared from dispersions containing alumina and phosphoric acid was controlled by the relative amount of acid and hence relative amount of aluminum phosphate. The addition of aluminum chloride to the dispersion led the formation of fine aluminum hydroxide precipitates that react with phosphoric acid at lower temperatures to form aluminum phosphate reaction products; these fine reaction product help to bind the alumina particles together and thus lower the processing temperature. The success of this low-temperature phosphate route leads to the possibility of other coating systems utilizing alternate sources of phosphate which require less harsh conditions (pH, etc...) and which may be more widely applicable to a variety of substrates. More details on this research can be found in a technical report.

## PUBLICATIONS

Y. J. Kim and L. F. Francis, "Processing and Characterization of Porous Titania Coatings," *J. Amer. Ceram. Soc.*, **76** [3] 737-42 (1993).

Y. J. Kim, N. M. Wara, B. V. Velamakanni, and L. F. Francis, "Microstructure Development in Particulate Ceramic Coatings," *Ceramic Transactions*, Vol. 43, Ferroic Materials: Design, Preparation, and Sensor Characteristics, 183-195 (1994).

Y. J. Kim, "Sol-Gel Processing and Characterization of Macroporous Titania Coatings," Ph.D. Thesis, University of Minnesota, 1995.

B. D. Craig, L. F. Francis, and L. Abrams, "Measurement of Porosity in Ceramic Coatings by Thermogravimetric Volatilization of Liquids," *J. Amer. Ceram. Soc.*, **79**[12] 3317-20 (1996).

B. D. Craig and L. F. Francis, "Development and Control of Porosity in  $\text{Al}_2\text{O}_3/\text{AlPO}_4$  Coatings," Technical Report (1997).

Y. J. Kim and L. F. Francis, "Microstructure and Crystal Structure Development in Porous Titania Coatings Prepared from Anhydrous Titanium Ethoxide Solutions" submitted to *J. Materials Science* (1997).

**REPORTABLE INVENTIONS**

Low Temperature Fabrication of an Interpenetrating Phase Composite Coating, Invention Disclosure, November 1996.

**SCIENTIFIC PERSONNEL**

Young-Joo Kim, PhD. 1995

Bradley D. Craig, PhD candidate.

Yaquing Ming, post-doc (January 1996)